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Sustainable leaching of critical metals from lithium ion battery black mass using a citric acid and choline chloride deep eutectic solvent

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Abstract
The recycling of lithium-ion batteries (LIBs) is of critical importance due to the increasing demand for electric vehicles and portable electronic devices. It also helps address supply risks of critical raw materials and reduces the environmental impact of mining. Traditional recycling methods are often inefficient and environmentally damaging. This study investigates the use of deep eutectic solvents (DES), made from citric acid and choline chloride, for leaching valuable metals from black mass derived from spent LIBs. The research focuses on optimizing the leaching parameters, such as temperature, DES ratio, and solid-to-liquid ratio, to maximize the extraction efficiency of lithium, cobalt, nickel, and manganese. A key aspect of the study was the examination of the rheological properties of the DES system, as these properties significantly impact the leaching process. The viscosity and pH of the DES were measured, providing insights into their behavior under various conditions. Understanding the viscosity and flow characteristics of these DES systems is crucial for developing scalable and effective recycling methods. The DES mixture with a 2:1 ratio of citric acid to choline chloride, mixed with 50% water, showed the best performance. At 90 °C for 24 h, this DES mixture achieved leaching efficiencies of 77.5% for lithium, 79.9% for cobalt, 80% for manganese, 66.2% for nickel, 82.5% for copper, and 93.8% for aluminum. These findings suggest the potential of citric acid-choline chloride DES as a sustainable and environmentally friendly reagent for recycling LIBs.

Keywords Battery, Lithium-based black mass recycling, Deep eutectic solvents (DES), Leaching, Critical metal recovery

1 Introduction

The rapid growth in the use of lithium-ion batteries (LIBs) in electric vehicles and portable electronic devices has led to a significant increase in spent batteries, creating a pressing need for efficient and environmentally friendly recycling methods [1, 2]. Recycling can be performed via two major methods. Pyrometallurgy techniques are energy-intensive operations that necessitate costly gas treatment, generate large volumes of waste, and are inefficient in recovering Li, which is typically lost in the slag alongside Mn and Al [3–6]. In contrast, hydrometallurgy techniques are more flexible, associated with low energy consumption and allow the recovery of Li, Al, and Mn [3, 4]. Processes start with the dissolution of the metal from the cathode material in acidic media. This is usually done via strong inorganic acids such as H_2SO_4, HCl and HNO_3. Hydrogen peroxide (H_2O_2) acts as a reducer to decrease the oxidation state of some metals (for example Co^{3+} to Co^{2+}) and improves their leachability, though it easily decomposes, limiting its efficiency. Although hydrometallurgy has advantages, it can also cause environmental impacts, since it requires large amounts of water, releases gases, produces secondary pollution, and requires corrosion-resistant equipment [7, 8].

In recent years, deep eutectic solvents (DESs) have emerged as a promising alternative for metal recovery from various waste streams due to their unique properties, such as low volatility, high thermal stability, and tunable solubility [9–12]. DESs are typically composed of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), which, when mixed, form a eutectic mixture with a melting point much lower than that of the individual components [13, 14].

Among the various DESs, citric acid-choline chloride has shown particular promise for its effectiveness in metal leaching applications. Citric acid, as an organic acid, provides strong complexation abilities, indeed the citrate ligand formed by hydrogen dissociation can form strong complexes with cationic metals. While choline chloride, a cheap organic salt, enhances the solubility and stability of the DES [15, 16]. It is worth mentioning that cationic metals could also be complex with the chlorine ion. A research paper investigated the synthesized citric acid monohydrate-choline chloride-based DES and characterized their physicochemical properties, including density, viscosity, and surface tension at different temperatures. They found that a higher ratio of citric acid resulted in higher density, viscosity, and surface tension, while a higher ratio of choline chloride increased the melting point of the DES. This insight is critical for tailoring DES formulations to specific recycling needs, ensuring both efficiency and sustainability [16].

Previous studies have demonstrated the potential of citric acid-choline chloride DES in the recovery of valuable metals from spent LIBs, achieving high leaching efficiencies under mild conditions [17–20]. A study examined the pH behavior of seventeen different aqueous DES combinations, including citric acid-choline chloride (CA-ChCl), across a temperature range of 25–60 °C. The solvents were tested in various ratios diluted to 0.5 mol/L. It was found that the pH of the oxalic acid-choline chloride (1:1) DES showed the highest temperature dependency, while the citric acid-choline chloride (2:1) DES exhibited the least temperature dependency [20]. In another study, CA-ChCl mixture diluted with water (i.e. CA: ChCl, molar ratio 1 : 1, diluted with 20 wt% water) was used to recycle LiCoO2-type cathode based black mass, and the optimized leaching conditions where more than 98% cobalt(II) recovered were recorded as 60 min of leaching at 40 °C with a solid to liquid ratio of 20 g/L [19]. These findings highlight the stability and suitability of citric acid-choline chloride DES for use in varying thermal conditions, which is advantageous for recycling applications.

We have previously conducted a preliminary study involving the experimental selection and characterization of various deep eutectic solvents (DESs), as reported by

Strömberg [21]. In that work, DESs composed of organic acids and chloride-based salts were investigated for the recovery of valuable metals from lithium-based black mass. The organic acids used were citric acid monohydrate, oxalic acid dihydrate, and malic acid, which were combined with chloride salts including ammonium chloride, aluminum chloride hexahydrate, choline chloride, and tetramethylammonium chloride in molar ratios of 1:1, 1:2, and 2:1. Twelve DES combinations were characterized in terms of pH and optical viscosity to identify solvents with low acidity and viscosity. The selected DESs were subsequently applied in leaching experiments targeting nickel, cobalt, and manganese from black mass materials with NMC 111 and NMC 622 cathode structures. Leaching parameters, including temperature (60–150 °C), solvent ratio, solid-to-liquid ratio, and duration were systematically optimized. Kinetic studies further evaluated the effect of leaching time on metal extraction efficiency. Among the tested DESs, the combination of citric acid and choline chloride exhibited the highest potential for efficient metal recovery.

An important and distinctive aspect of this research is the comprehensive investigation of the rheological properties of DES, particularly their viscosity and flow behavior. These properties are crucial because they influence the mass transfer rates and the overall efficiency of the leaching process [22]. Higher viscosity can hinder the movement of ions and reduce the contact between the solvent and the metal particles, thereby affecting the leaching efficiency. Conversely, lower viscosity facilitates better flow and mixing, enhancing the leaching process [23]. Understanding these properties allows for the optimization of the DES formulation and processing conditions, ensuring effective and scalable recycling methods. This study aims to explore the use of citric acid-choline chloride DES for the selective recovery of lithium, cobalt, nickel, and manganese from the black mass of spent LIBs.

The novelty of this work lies in coupling leaching optimization with a detailed rheological analysis of the DES and in elucidating the effect of water incorporation on viscosity and metal recovery efficiency. Introducing controlled amounts of water significantly decreases viscosity, thereby improving mass transfer and facilitating the practical application of DES in leaching. The findings of this research could contribute to the advancement of green chemistry approaches in the recycling industry, promoting the circular economy and reducing the environmental impact of battery waste.

2 Experimental

2.1 Materials and methods

The materials used in this study include citric acid monohydrate (98%) and choline chloride (99%) purchased from VWR BDH chemicals. Black mass from recycling of a battery pack with an NMC622 cathode ($LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$) was provided by Hydrovolt AS, Norway.

2.2 Black mass characterization

The elemental composition of the black mass was characterized using an Agilent 5800 inductively coupled plasma–optical emission spectrometry (ICP-OES). Prior to conducting the ICP-OES analysis, a specific digestion procedure was employed to ensure accurate results. In this procedure, a 0.3 g sample of black mass was dissolved in 30 mL of aqua regia (i.e., a concentrated acid mixture containing HCl/HNO_3 in a 3:1 volume ratio - using Emsure Supelco Hydrochloric acid 37% w/w and Emsure Supelco Nitric acid 65% w/w) at approximately 107 °C for 3 h. Following digestion, the slurry produced was filtered, and the filtrate was subsequently analyzed by ICP-OES.

XRD data were collected on a Bruker D2 Phaser with LynxEye XE detector and Cu K-alpha radiation. The powders were packed in a 2 mm deep specimen holder and data were collected over a 2-Θ range of 5-100 ° with a step size of 0.02 ° and a count time of 0.7 s/step. The crystalline phases were identified using the crystallography open database (COD) in Bruker EVA version 6.0.0.7. Quantitative analysis (QPA) was carried out with TOPAS V7 over the angular range from 12 to 100 deg. A fundamental parameters peak shape derived from the D2 Phaser geometry was used. The background was fitted with a 3rd order Chebyshev polynomial and the amorphous component was fitted with a broad peak with refined position, area and Lorentzian crystallite size. The crystalline phases were fitted using the Rietveld method with refined scale factors, lattice parameters and Lorentzian crystallite size. The amorphous content was determined using the total integrated area of the refined phases. Small unidentified peaks at 42.4, 77.5 and 83.6 ° 2-Θ were fitted with a single crystallite size parameter and individual position and area parameters and flagged as crystalline components for amorphous content determination. The amorphous content was estimated from a broad peak at 23 ° 2-Θ fitted with crystallite size, position and area parameters.

2.3 Rheological analysis of studied DES

Rheological analysis was conducted to characterize the rheological properties of the samples. Anthon Paar MCR702e, twin drive, was employed which was equipped with disposable plate-plate configuration with diameter of 25 mm; it is made of aluminum. Since the fluids were thick and pasty at room temperature, it was decided to study the shear behavior of the samples at a low shear rate of 1 s^{-1}. The characterization was decided to be conducted in a temperature range of 20–120 °C and ambient pressure. The temperature ramp-up rate selected for this study was 1 °C/min. The upper temperature limit was decided due to the results obtained in the screening phase where fluid evaporation from the samples becomes a concern. The characterization decided to present in this work is the effect of temperature on viscosity of the afore-mentioned samples.

2.4 Leaching procedure

For the experiments, a simple leaching setup was used that consists of a round three neck flask heated in an oil bath with integrated stirrer and condenser. DES mixtures were prepared by mixing citric acid monohydrate (CA) and choline chloride (ChCl) in the ratios of 1:1, 1:2, and 2:1. These mixtures were heated in an oil bath with continuous stirring at 300 rpm and at 90 °C for 30 min. Temperature was gradually increased from 25 °C to 100 °C to observe phase changes and determine the melting points. The pH was measured using a sensION TM + PH31 pH meter from HACH, calibrated regularly.

The leaching experiments were conducted using the three CA-ChCl based DES combinations with 50 ml of the selected DES in an Erlenmeyer flask at relevant temperature with continuous stirring for at least 30 min. Subsequently, 50 mL of DES was transferred to a round-bottom flask, and 2.5 g of black mass was also added to the flask to achieve the designated solid-to-liquid ratio (S/L). The leaching process was then carried out at different temperatures (i.e. 60, 90, 120, 150 °C) for two hours. Afterward, the leaching slurries were filtered and analyzed for calculating the extraction yields of Ni, Mn, Co, and Li.

The best performing DES from the initial leaching experiments were selected for further investigation and kinetic study. A kinetic study was conducted at two different temperatures (90 °C and 150 °C) with a S/L of 50 g/L. Leaching duration was set at 1, 2, 4, 6, 18, and 24 h to investigate the effect of time on leaching efficiency. Afterward, the leaching slurries were filtered and analyzed to determine the concentrations of Ni, Mn, Co, and Li.

The leaching efficiency of metal *i* (Yi) in the solution was calculated using Eq. (1)

$$Yi\,(\%) = \frac{C_{i,l} \times m_l}{C_{i,BM} \times m_{BM}} \times 100\% \tag{1}$$

where $Ci_{,l}$ is the concentration of a metal *i* in the leachate (mg/kg), m_l is the mass of the leachate (kg), $Ci_{,BM}$ is the concentration of a metal *i* in the black mass sample (mg/kg), and m_{BM} is the mass of the black mass sample used in leaching (kg).

To reduce viscosity, certain DES mixtures-specifically the 2:1 CA: ChCl formulation-were prepared with 50 wt% deionized water and used as leaching agents in 24-hour tests. The outcomes were then compared to those from CA: ChCl mixtures without added water at both 90 °C and 150 °C.

3 Results and discussion

3.1 Black mass characterization

The results from the analysis of the black mass sample provided a detailed understanding of its elemental composition, phase structure, and transformations following treatment with the citric acid-choline chloride DES system. Initial characterization of the black mass, conducted using an Agilent 5800 inductively coupled plasma optical emission spectrometry (ICP-OES), provided the concentration of main elements such as nickel, manganese, cobalt, and lithium (Table 1), and present impurities.

To further investigate the crystalline structure and composition, X-ray diffraction (XRD) analysis was performed on the black mass both before and after the extraction process. Seven distinct crystalline phases were identified in the initial black mass, and these phases were quantified using Rietveld analysis, with the crystalline-to-amorphous ratio calculated for each sample. Differences in composition, crystallinity, and phase distribution before and after DES leaching underscore the selective recovery capabilities of the DES system and its impact on the structure and distribution of valuable metals within the black mass.

Table 1 Elemental composition of the black mass sample (wt%) as determined by ICP-OES analysis

Composition	Weight (%)	Relative Standard Error (%)
Ni	13.64	2.76
Mn	4.36	3.45
Co	4.47	2.54
Li	2.56	3.13
Cu	2.42	1.12
Al	1.12	1.47
Fe	0.005	2.27

3.2 Rheological properties

The viscosity-temperature relationship of citric acid-choline chloride (CA) deep eutectic solvent (DES) mixtures was investigated across a range of temperatures and molar ratios. Viscosity is important during the leaching to ensure the efficient interaction between solid and liquid species. This investigation provides insights into the suitability of each DES formulation for scalable applications in black mass recycling. As shown in Fig. 1, viscosity measurements were conducted for DES systems with varying ratios of citric acid to choline chloride (1:1, 1:2, and 2:1) and tests were repeated three times for each mixture. The study reveals a distinct inverse relationship between viscosity and temperature for all DES formulations, with viscosity decreasing as temperature increases from room temperature to 120 °C.

The results obtained reveal that the CA: ChCl 1:1 ratio exhibits the highest viscosity across the selected temperature range. When comparing the viscosity profiles at room temperature, the viscosity of this sample is an order of magnitude higher, ten times greater than that of the CA: ChCl 2:1 ratio. A similar observation holds true for the CA: ChCl 2:1 ratio compared to the CA: ChCl 1:2 ratio. The 1:2 and 2:1 ratios displayed comparatively lower viscosities at each temperature, suggesting that the balance between citric acid and choline chloride or water content due to the hygroscopic nature of the DES affects the fluidity.

As the temperature increases, the CA: ChCl 2:1 sample experiences a much faster reduction in viscosity compared to the other two samples; however, this trend is valid only up to 90 °C. Upon reaching 90 °C, the viscosity profile of CA: ChCl 2:1 begins to increase. Various hypotheses can be proposed to explain this behavior, such as the decomposition of the solvent mixture, initiation of a consecutive reaction, or the flow of fluid outside the disposable plates, creating an end effect. However, this behavior was not observed for the other samples. This needs further investigation.

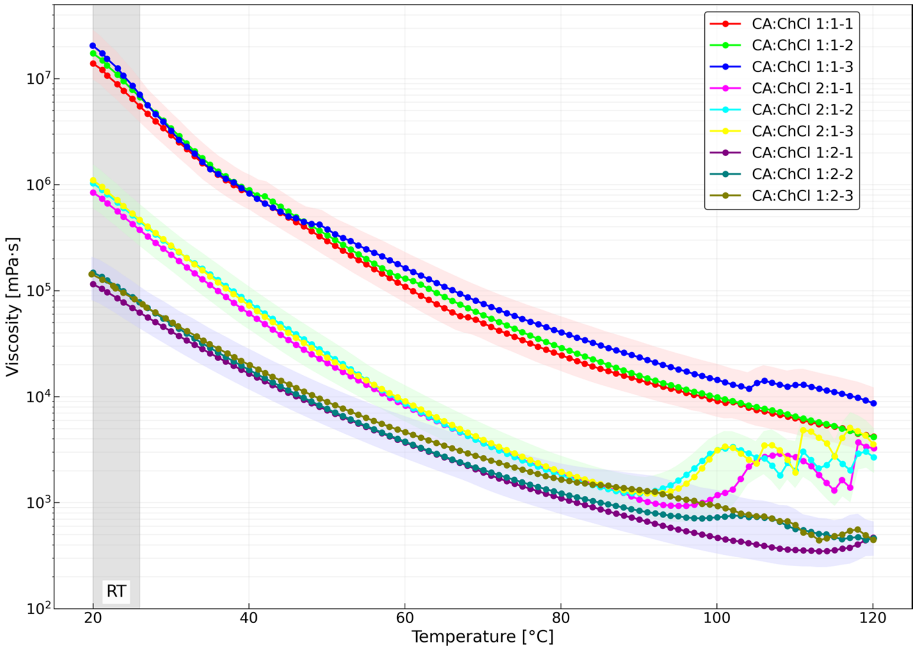

Fig. 1 Viscosity vs. Temperature for different CA: ChCl ratios

From the measurements, it is evident that the viscosity of all samples decreases significantly as the temperature rises. The significant drop in viscosity with temperature suggests that elevated temperatures are favorable for reducing resistance to flow, which can facilitate the leaching process by enhancing the interaction between the DES and the black mass particles. Notably, at the optimized leaching temperature of 90 °C, all DES mixtures achieved manageable viscosities suitable for practical application.

In general, we observed that the viscosity of CA-ChCl system decreases as the choline chloride content increases which was consistent with the literature. However, when citric acid increases, we observed also a decrease in the viscosity which contrasts with reports in the literature suggesting that higher citric acid content increases viscosity [16, 24]. Typically, the higher viscosity of CA-ChCl is attributed to the polyfunctional nature of citric acid, which forms a dense hydrogen bonding network [25]. However, water content in the DES can significantly impact viscosity and performance. Citric acid's three carboxyl groups enable it to attract and retain water molecules through extensive hydrogen bonding networks. Literature reports that CA-ChCl 1:1 system exhibit some water content (around 7.42%), which proves naturally existing hydrogen bonding sites that retain water [26]. This retained water can act as a co-solvent, disrupting the hydrogen bonding network and reducing viscosity. This behavior could explain our observation of decreasing viscosity with increasing citric acid content as our study was not conducted under controlled atmospheric conditions. This decision was intentional, as the study was designed to ensure that the process would be easily adaptable to industrial applications. The observed viscosity reduction in our setup, influenced by environmental moisture, reflects practical conditions, providing a more realistic understanding of the system's behavior and its potential for industrial applications.

3.3 Recovery yield of target elements with studied DES

Figure 2 presents the leaching efficiencies of nickel (Ni), manganese (Mn), cobalt (Co), and lithium (Li) across four temperatures (60 °C, 90 °C, 120 °C, and 150 °C) for three different molar ratios of citric acid to choline chloride (1:1, 2:1, and 1:2). The data indicate that both temperature and ratio significantly influence metal recovery rates, with distinct trends observed for each metal.

As shown in Fig. 2a, nickel leaching efficiency was generally low across all conditions but showed a slight increase with temperature. The 2:1 displayed the highest efficiency at 90 °C, reaching approximately 25%, after which the efficiency plateaued. The reason may be attributed to that most likely the reaching a suitable viscosity values before observing some viscosity changes in the solvent system such as the decomposition of the solvent mixture. The 1:1 exhibited more stable but lower recovery rates across the temperature range, while the 1:2 showed minimal recovery efficiency, suggesting that nickel extraction is less favored under these conditions. This behavior may be also attributed to the nickel forming stable complexes with citrate ions, where the higher citric acid content in 2:1 ratio facilitates complexation and enhances dissolution at moderate temperatures. The complexolysis mechanism of citric acid with Ni and other transitional metals is given below via Eq. (2) [27].

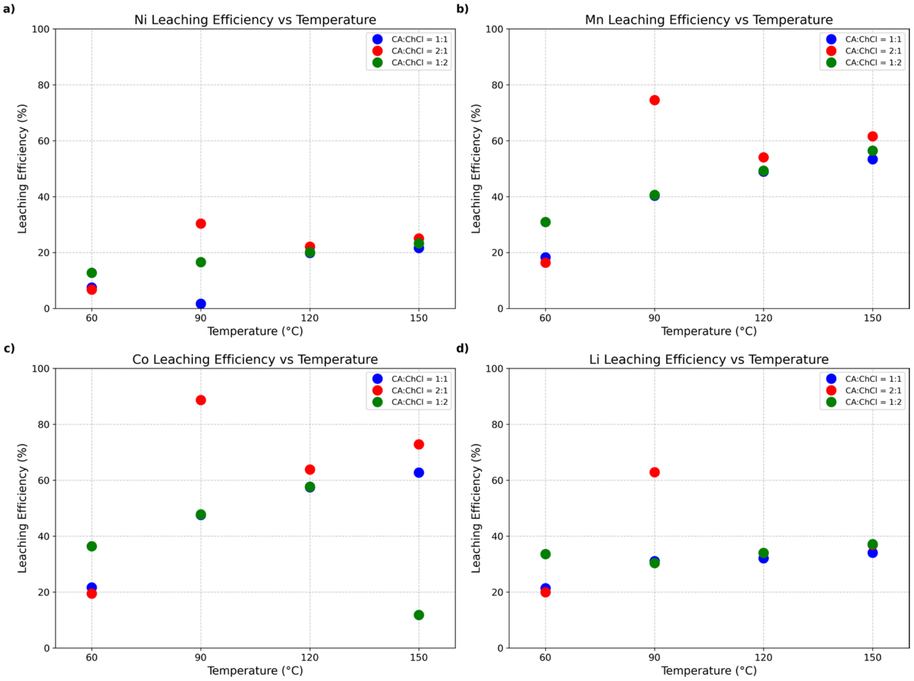

Fig. 2 The leaching efficiency of **a** Ni, **b** Mn, **c** Co, and **d** Li at four different temperatures (i.e., 60 °C, 90 °C, 120 °C, and 150 °C) for three CA: ChCl ratios (i.e., 1:1, 2:1, and 1:2) and for 2 h

$$C_6H_8O_7 \rightarrow \left\{ \begin{array}{l} C_6H_7O_7^- + H^+ \\ C_6H_6O_7^{2-} + H^+ \\ C_6H_5O_7^{3-} + H^+ \end{array} \right. + M^{n+} \rightarrow \begin{array}{l} M[C_6H_7O_7]_n \\ M_2[C_6H_6O_7]_n \\ M_3[C_6H_5O_7]_n \end{array} \tag{2}$$

Figure 2-b, manganese leaching efficiency increased significantly with temperature, particularly for the 2:1, which achieved the highest recovery of around 80% at 90 °C. This efficiency slightly decreased at 120 °C and 150 °C but remained significantly higher than the other ratios. Both the 1:1 and 1:2 showed moderate efficiencies, peaking at 90 °C and then stabilizing, indicating that manganese recovery is optimal at moderate temperatures with a 2:1. The high efficiency of manganese recovery under 2:1 ratio may result from the higher acidity and strong complexing ability of citric acid, promoting the dissolution over the highly soluble complex formation. The citrate ions further stabilize Mn ions through complexation, ensuring their solubility via Eq. (2).

Figure 2-c shows that cobalt recovery was most efficient with the 2:1, achieving a peak leaching efficiency of over 90% at 90 °C. This efficiency decreased at higher temperatures, with a notable drop at 150 °C. The 1:1 and 1:2 ratios produced lower efficiencies across the temperature range, with only minor improvements at elevated temperatures. These results suggest that cobalt is most effectively extracted at 90 °C with a 2:1 DES ratio, as higher temperatures do not favor further improvement in recovery. Similar to Ni and Mn cases, Co also most likely formed soluble complexes via Eq. 1 that gives ideal conditions at 90 °C where stability of the most soluble complex is favorable. Considering Ni, Mn and Co complexes, it is known that the order of the stability constants increases from Mn to Co and then finally Ni that means that dipositive metal ion complexes follow the Irving-Williams stability series [28]. However, Ni shows lower leaching yields compared to Co and Mn in our study. The reason for this might be the different oxidation

states of these transitional metals in the cathode structure as it is known that the oxidation state might affect the stability and solubility of the complexes [29].

Lithium leaching efficiency (Fig. 2-d) followed a different pattern, with the 2:1 again demonstrating the highest recovery, peaking at approximately 45% at 90 °C. However, unlike the other metals, lithium leaching efficiency did not show substantial increases at higher temperatures, and recovery remained relatively constant across the temperature range. The 1:1 and 1:2 produced lower and stable efficiencies, indicating limited temperature dependence for lithium extraction. Overall, the 2:1 at 90 °C consistently provided the highest leaching efficiencies for Mn, Co, and Li, with varying degrees of success for Ni. These findings highlight the importance of optimizing both temperature and DES composition to maximize the recovery of each target metal, particularly with the 2:1 at moderate temperatures being most effective for efficient metal leaching that was also reported in the literature previously [19].

Overall, the observed increase in leaching efficiency around 90 °C, followed by a decline at higher temperatures, can be explained by the influence of temperature on reaction kinetics and the stability of the system. At 90 °C, the reaction rates are sufficient to enhance lattice breakdown and the dissolution of metals, leading to higher recovery rates [30]. At higher temperatures, such as 150 °C, competing reactions might accelerate or changes in the behavior of the DES can occur, such as altered viscosity or reduced complex stability. These factors could limit the recovery rates, even though they might result in faster initial kinetics, as explained below in the kinetics section.

3.4 Leaching mechanism

The black mass used in this study primarily consists of transition-metal oxides, where lithium occupies interstitial sites within a layered oxide lattice, and Ni, Mn, and Co are present in octahedral coordination with oxygen. These oxides are chemically stable and require both proton attack and complex formation to break the metal-oxygen framework effectively.

Mechanically, the leaching process can be described as a proton-assisted complexolysis reaction governed by the interplay between acidity, complex stability, and solvent viscosity. At moderate temperatures (~ 90 °C), the DES exhibits optimal viscosity, allowing efficient diffusion of protons and citrate ligands to the cathode surface. This facilitates metal–oxygen bond cleavage and subsequent complexation with citrate ions. The effect is most pronounced for the 2:1 CA-ChCl ratio, where higher citric acid content enhances both proton availability and chelation capacity. The high leaching efficiency of cobalt (≈ 90%) and manganese (≈ 80%) under these conditions suggests that both metals form soluble and moderately stable metal-citrate complexes, whereas nickel shows limited recovery (~ 25%) due to the formation of highly stable but less soluble complexes. Thus, the leaching selectivity follows the order Co > Mn > Ni, with a selectivity for cobalt over nickel of approximately ~ 3.6:1.

3.5 Leaching challenges of nickel-rich NMC cathodes

Nickel-rich NMC-type cathodes are characterized by their high energy density and thermal stability, making them suitable for high-performance lithium-ion batteries [31]. However, the presence of nickel in higher oxidation states within these cathodes contributes to the formation of stable oxides or mixed oxides, which are not readily soluble under mild acidic conditions [32]. Additionally, lithium is incorporated within stable layered oxide lattices, which restricts its release during mild leaching processes, further complicating the extraction of metals from these cathodes [33]. Organic-acid-based deep eutectic solvents (DESs) facilitate metal dissolution primarily through protonation and the formation of stable metal-ligand complexes, rather than relying on oxidative dissolution mechanisms typical of mineral acids [34]. This mechanism leads to slower kinetics and reduced leaching rates [35]. In addition, the relatively high viscosity of DES, especially at low water content can impede ion diffusion and hinder solid–liquid interactions, thereby reducing dissolution rates [13].

3.6 XRD and quantitative phase analysis of black mass

Black mass was analyzed with XRD before and after the DES extraction process. Seven crystalline phases were identified in the black mass, as shown in Table 2, and were used in quantitative Rietveld analysis (QPA). Three small peaks from crystalline material at 42.4, 77.5 and 83.6 ° 2-Θ were fitted individually (pks phases in TOPAS) for use in the crystalline content determination but not used in the QPA. These peaks are labelled in Fig. 3. The agreement factors for the fits to the data before and after leaching were Rexp : 1.95, Rwp : 5.14, GOF : 2.63 (before) and Rexp : 3.64, Rwp : 11.54, GOF : 3.17 (after). Full results of the fitting are given in the Annex I. Supplementary Information.

The XRD pattern before extraction had a crystalline area of 48382.544 (including the peaks from the unidentified phase) and an amorphous area of 3584.929, giving a degree of crystallinity of 93.1%. After extraction the crystalline area was 23813.054 vs. an amorphous area of 12796.471, giving a 65.05% degree of crystallinity.

The results show significant loss of LiNMC after the extraction process along with a small loss of Cu and Al, the fractions of which we might expect to have increased relatively on removal of the main crystalline component. Some of the Al may have been converted to Gibbsite and Boehmite (the fractions of which increase) during the extraction process. The loss of crystallinity after extraction is consistent with the removal of the highly crystalline LiNMC phase.

3.7 Leaching kinetics

Figure 4 presents the leaching fraction, X(t), for nickel (Ni), manganese (Mn), cobalt (Co), and lithium (Li) over time at two temperatures: 90 °C and 150 °C normalized to the initial metal content. The use of t-X(t) differs from the overall leaching efficiency representation, as it focuses on the rate and mechanism of leaching over time rather than cumulative recovery. The results show a clear temperature dependency in the leaching

Table 2 Results of XRD quantitative analysis of the crystalline part of the black mass sample, estimated standard deviations in the final digit of the weight percentages are given in brackets after the values

Phase name	COD number	composition	Weight% before leaching	Weight% after leaching
Graphite 2 H	1,200,017	C	23(1)	73.8(6)
LiNMC	4,002,443	$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$	61(1)	2.3(2)
corundum	9,009,783	Al_2O_3	5.0(3)	8.8(3)
copper	9,012,954	Cu	1.5(1)	1.2(1)
Aluminum	9,012,956	Al	2.4(2)	0.7(2)
Gibbsite	9,015,976	$Al(OH)_3$	4.6(2)	11.3(4)
Boehmite	9,012,275	AlO(OH)	1.8(3)	2.0(3)

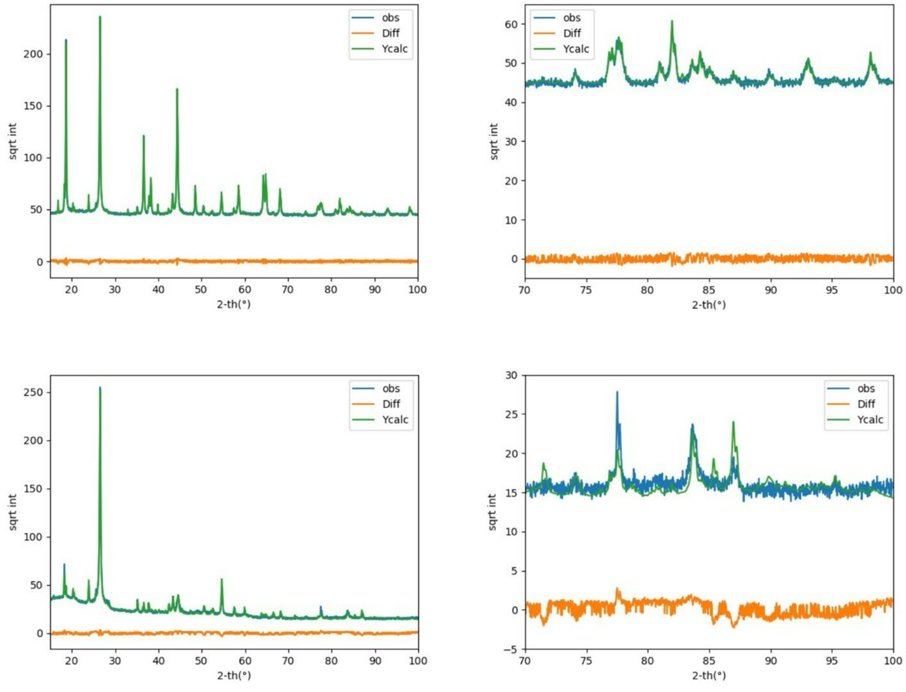

Fig. 3 Rietveld plots of the QPA fit results before (top) and after (bottom) leaching with 2:1 CA: ChCl at 90 °C for 48 h. The plots on the right are zoomed in to show the quality of fit at high angles. The y-axis scale is plotted on a square root scale to better show the weak peaks

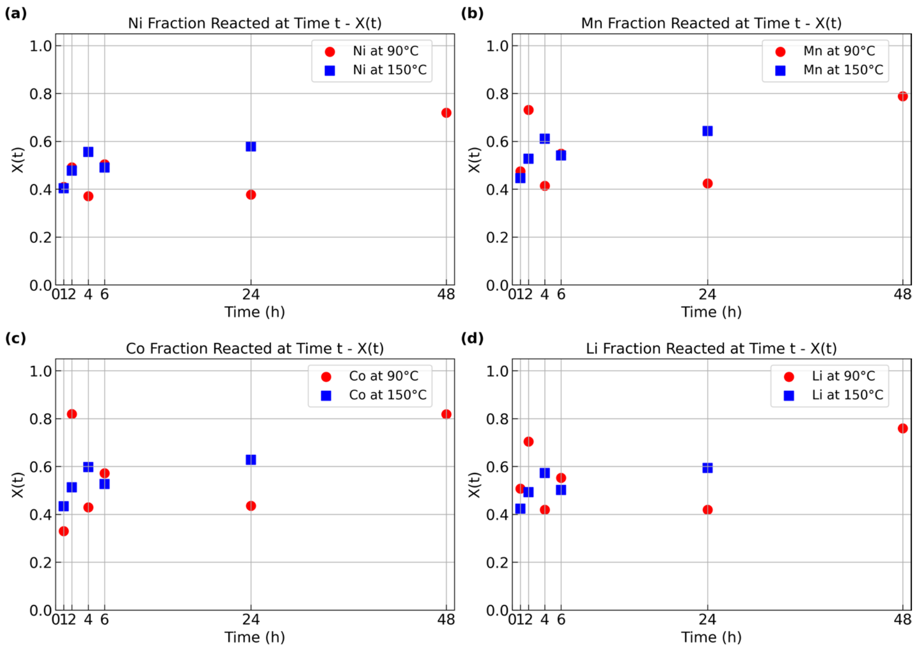

Fig. 4 The leaching efficiency of **a** Ni, **b** Mn, **c** Co, and **d** Li over time at two different temperatures (i.e., 90 °C and 150 °C) for CA: ChCl of 2:1

kinetics, with a higher temperature of 150 °C significantly enhancing both the rate and extent of metal recovery across all elements compared to 90 °C.

At 150 °C, a rapid initial leaching was observed, with reaction fractions approaching 0.7–0.9 within the first 6 h, and gradually plateaued over time. This behavior supports the hypothesis that higher temperatures accelerate the metal dissolution process, allowing for more efficient extraction within a shorter timeframe. The leaching yield for all metals continued to rise slightly beyond 24 h at 150 °C, suggesting that extended leaching times could further improve recovery, though the rate of increase diminishes as equilibrium is approached.

In contrast, at 90 °C, the leaching yield for all metals was notably lower and reached a plateau much earlier, stabilizing around 0.4–0.5 after 24 h which was also expected. This indicates that the leaching process is slower and less efficient at lower temperatures, as lower thermal energy reduces the rate of dissolution. The results demonstrate that 150 °C provides optimal conditions for maximizing metal recovery rates, achieving significantly higher extraction efficiencies compared to 90 °C. However, at such high temperatures, even though a flux condenser to help reduce evaporative losses was employed, some water loss is inevitable.

On the other hand, this might be due to the decomposition of deep eutectic solvents that might assist further metals extraction [36]. The decomposition of the solvents, hence the higher the leaching at higher temperatures is not desired as it might prevent the reuse of the solvents [37] and increase the energy demand of the process.

While kinetic models are often applied to analyze leaching processes, we did not further investigate model fitting in this study due to the limited number of data points and variability in the experimental results. Although we explored applying kinetic models to analyze the leaching process, the models tested did not provide a good fit to the experimental data. The complexity of the system, which likely involves competing chemical processes such as diffusion, surface reactions, and potential re-deposition or precipitation of dissolved species, would require a more detailed dataset to yield meaningful and robust kinetic interpretations. Instead, we focused on descriptive trends observed in the raw data, which provide valuable insights into the time-dependent behavior of metal dissolution under the tested conditions. High viscosity in the deep eutectic solvent (DES) system likely contributed to slower solid-liquid interactions, which could influence the leaching kinetics by limiting mass transfer at the interface. This effect introduces variability in experimental data and complicates the identification of a consistent rate-limiting mechanism, such as diffusion or chemical reaction control. These factors, combined with the limited number of data points, made it difficult to achieve reliable fits with conventional kinetic models.

Figure 5 shows the effect of water addition to the DES mixture. The results highlight that adding water and keeping the leaching temperature at 90 °C improves leaching efficiency even more than increasing the temperature to 150 °C. Water addition significantly reduces the viscosity of the DES, making it less thick and allowing the leaching process to proceed more efficiently. This lower viscosity enhances mass transfer, allowing metals to dissolve more easily. As a result, leaching efficiencies at 90 °C with water exceed those achieved at 150 °C without water for all metals, showing that water addition can effectively boost performance without needing higher temperatures.

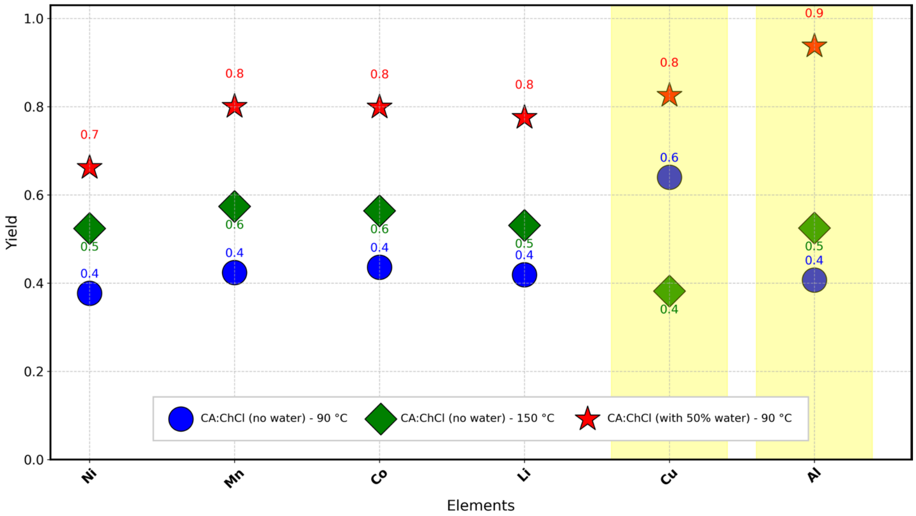

Fig. 5 Comparisons of the leaching efficiencies of Ni, Mn, Co, Li, Cu, and Al over 24 h under different viscosity conditions

The presence of water in the DES, both naturally retained due to its hygroscopic nature and through deliberate addition, significantly affects viscosity and plays a crucial role in improving mass transfer and enhancing extraction efficiency. The hygroscopic character of the CA-ChCl system allows it to naturally attract and retain water molecules, which disrupt the dense hydrogen bonding network and reduce internal friction. This inherent water retention already contributes to lower viscosity and better performance at higher citric acid content. Adding additional water to the DES amplifies this effect, further reducing viscosity and enabling more efficient extraction processes. These findings highlight the complex dynamics of CA-ChCl systems and emphasize the importance of optimizing both composition and water content, leveraging the hygroscopic nature of DES to enhance their applicability in open and industrially relevant conditions.

An additional advantage of using water is the possibility of evaporating it after the leaching process to recover the target elements, as the solubility of each component varies. This approach could make the process more sustainable and economical, as water could be reused after separation. Further study is needed to optimize this recovery step, but the results give a strong indication that water addition is a promising strategy. This finding suggests that water addition is a practical way to enhance metal recovery while keeping the process energy-efficient and scalable.

4 Prospective studies on CA: ChCl regeneration

A recent review by Svärd, et al. [37] compiled several studies demonstrating that choline chloride–based DESs can be effectively regenerated and reused. In particular, systems based on choline chloride with lactic acid have shown stable performance for up to four reuse cycles, while choline chloride–oxalic acid DESs have maintained leaching efficiency over three to five consecutive uses without significant compositional degradation. These findings confirm that regeneration and reuse of DESs are feasible. However, experimental data for choline chloride–citric acid (CA: ChCl) systems remain limited. To date, Yu, et al. [38] have provided the only detailed study assessing the reusability of CA: ChCl, demonstrating that the solvent maintained high copper leaching efficiencies of 98.43%, 95.48%, and 94.74% over three consecutive cycles, with complete metal recovery via electrodeposition in each case.

5 Potential downstream processing steps following leaching

After leaching, the solution typically contains a mixture of metals along with impurities such as aluminum and iron, necessitating effective purification. Chemical precipitation is commonly employed as an initial recovery method, where adjusting the pH selectively removes impurities as hydroxides, enriching the solution in target metals [39]. Nickel, cobalt, and manganese are usually precipitated before lithium using specific precipitants such as NaOH or Na_2CO_3 [40]. Copper and aluminum recovery can also be achieved through careful pH control and precipitant selection. Solvent extraction further refines separation, selectively extracting metals such as cobalt and nickel from the aqueous phase using appropriate organic extractants [39].

For metal recovery, purified metals can be retrieved via electro-deposition, depositing ions like cobalt and nickel onto electrodes under controlled electrochemical conditions [39, 41], and lithium is typically recovered through crystallization as lithium carbonate from purified solutions [42].

6 Conclusions

This study demonstrates that a citric acid and choline chloride-based deep eutectic solvent (DES) in a 2:1 ratio, with 50% water, provides an efficient and environmentally friendly method for black mass recycling. Under optimized conditions of 90 °C for 24 h, high leaching efficiencies for lithium, cobalt, manganese, and nickel were achieved, at approximately 77.5%, 79.9%, 80%, and 66.2%, respectively. These recovery rates highlight the potential of this DES system for sustainable metal recovery.

The addition of water in the DES formulation appeared to reduce viscosity and improve recovery yields, addressing one of the challenges in DES-based recycling processes. For the selective recovery of leached metals, precipitation with targeted chemical additives or through direct water evaporation/distillation may be feasible approaches.

Future studies should explore the decomposition pathways of citric acid and choline chloride under high-temperature conditions to determine any possible release of volatile, potentially toxic compounds. While this study did not focus on this aspect, stability of the mixture was confirmed at 90 °C, the primary temperature used in this work.

Overall, this research supports the effectiveness of a citric acid-choline chloride DES as a more environmentally friendly alternative for black mass recycling compared to the traditional inorganic acids and points to the need for continued optimization and safety assessment.

Supplementary Information

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Supplementary Material 1

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Author contributions

Fernando Sitorus 1 : Conceptualization, Methodology, Software, Validation, Formal Analysis, Investigation, Writing–original draft, Writing–review and editing, Visualization. Elin Stromberg 2 : Methodology, Investigation, Data curation, Validation. Lea Rouquette 2 : Conceptualization, Methodology, Writing–review and editing. Kim Andre Nesse Vorland 3 : Methodology, Data curation, Formal Analysis. Mahmoud Khalifeh 3 : Methodology, Formal Analysis. David Wragg 1 : Methodology, Formal Analysis, Investigation, Writing-review and editing, Project administration. Martina Petranikova 2 : Methodology, Writing-review and editing, Supervision. Duygu Yilmaz 1 : Conceptualization, Methodology, Formal Analysis, Writing–review and editing, Supervision, Project administration.

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Data availability

All data supporting the findings of this study are included in the article. Additional data or information can be obtained from the corresponding author upon request.

Declarations

Competing interests

The authors declare no competing interests.

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References

1. Zhao Y, Pohl O, Bhatt AI, Collis GE, Mahon PJ, Rüther T, Hollenkamp AF. A review on battery market Trends, Second-Life Reuse, and recycling. Sustain Chem. 2021;2:167–205. https://doi.org/10.3390/suschem2010011.
2. International Energy Agency, Recycling of Critical Minerals: Strategies to Scale Up Recycling and Urban Mining. 2024, https://iea.blob.core.windows.net/assets/3af7fda6-8fd9-46b7-bede-395f7f8f9943/RecyclingofCriticalMinerals.pdf
3. Gaines L. Lithium-ion battery recycling processes: research towards a sustainable course. Sustain Mater Technol. 2018;17:e00068. https://doi.org/10.1016/j.susmat.2018.e00068.
4. Gaines L, Richa K, Spangenberger J. Key issues for Li-ion battery recycling. MRS Energy Sustain. 2018;5. https://doi.org/10.1557/mre.2018.13.
5. Larouche F, Tedjar F, Amouzegar K, Houlachi G, Bouchard P, Demopoulos GP, Zaghib K. Progress and status of hydrometallurgical and direct recycling of Li-Ion batteries and beyond. Materials. 2020;13. https://doi.org/10.3390/ma13030801.
6. Yun L, Linh D, Shui L, Peng X, Garg A, Le MLP, Asghari S, Sandoval J. Metallurgical and mechanical methods for recycling of lithium-ion battery pack for electric vehicles. Resour Conserv Recycl. 2018;136:198–208. https://doi.org/10.1016/j.resconrec.2018.04.025.
7. Li L, Ge J, Wu F, Chen R, Chen S, Wu B. Recovery of Cobalt and lithium from spent lithium ion batteries using organic citric acid as leachant. J Hazard Mater. 2010;176:288–93. https://doi.org/10.1016/j.jhazmat.2009.11.026.
8. Urias PM, Henrique dRML, Luiz CV, Maria dRM, J. and, de Souza, Ferreira. Leaching with mixed organic acids and sulfuric acid to recover Cobalt and lithium from lithium ion batteries. Environ Technol. 2021;42:4027–37. https://doi.org/10.1080/09593330.2020.1772372.
9. Zhu G, Chen Y, Wang S, Yang X. Deep eutectic solvents-based modern methods for metal extraction and recovery: current status, challenges, and perspectives. Sep Purif Technol. 2025;372:133382. https://doi.org/10.1016/j.seppur.2025.133382.
10. Wang C, Zhou Z, Zhang X, Guo H, Boczkaj G. Metal extraction using deep eutectic solvents for metal recovery and environmental remediation – A review. Sep Purif Technol. 2025;364:132533. https://doi.org/10.1016/j.seppur.2025.132533.
11. Chung Y-H, Sivasubramanian P, Chen C-L. Novel deep eutectic solvent systems for selective transition metal recovery and sustainable battery recycling. Sep Purif Technol. 2025;368:133098. https://doi.org/10.1016/j.seppur.2025.133098.
12. Tran MK, Rodrigues M-TF, Kato K, Babu G, Ajayan PM. Deep eutectic solvents for cathode recycling of Li-ion batteries. Nat Energy. 2019;4:339–45. https://doi.org/10.1038/s41560-019-0368-4.
13. Smith EL, Abbott AP, Ryder KS. Deep eutectic solvents (DESs) and their applications. Chem Rev. 2014;114:11060–82. https://doi.org/10.1021/cr300162p.
14. Fan Y, Kong Y, Jiang P, Zhang G, Cong J, Shi X, Liu Y, Zhang P, Zhang R, Huang Y. Development and challenges of deep eutectic solvents for cathode recycling of end-of-life lithium-ion batteries. Chem Eng J. 2023;463:142278. https://doi.org/10.1016/j.cej.2023.142278.
15. Hou YC. Deep eutectic solvents: green solvents for separation applications. Acta Phys -Chim Sin. 2018;34:873–85. https://doi.org/10.3866/PKU.WHXB201802062.
16. Shafie MH, Yusof R, Gan C-Y. Synthesis of citric acid monohydrate-choline chloride based deep eutectic solvents (DES) and characterization of their physicochemical properties. J Mol Liq. 2019;288:111081. https://doi.org/10.1016/j.molliq.2019.111081.
17. Wang B, Zhang Y, Zhu C, Ren S, Hou Y, Wu W. Advances of deep eutectic solvents in lithium battery recycling field. Sep Purif Technol. 2025;362:131836. https://doi.org/10.1016/j.seppur.2025.131836.
18. Zou J, Zhang R, Huang Y, Wang X, Chen L, Sun X, Wang M, Zhang Y, Wu K. High efficiency leaching of black powder from spent lithium-ion battery by ternary deep eutectic solvent and recovery of metals by precipitation and electrodeposition. Sep Purif Technol. 2025;364:132438. https://doi.org/10.1016/j.seppur.2025.132438.
19. Peeters N, Binnemans K, Riaño S. Solvometallurgical recovery of Cobalt from lithium-ion battery cathode materials using deep-eutectic solvents. Green Chem. 2020;22:4210–21. https://doi.org/10.1039/D0GC00940G.
20. Skulcova A, Russ A, Jablonsky M, Sima J. pH Behav Seventeen Deep Eutectic Solvents Biores. 2018;13:5042–51.

21. Strömberg E. Utilization of deep eutectic solvents (DES) in recovery of Li-based black mass. in, Chalmers University of Technology; 2024.
22. Jangir AK, Sethy P, Verma G, Bahadur P, Kuperkar K. An inclusive thermophysical and rheology portrayal of deep eutectic solvents (DES) for metal oxides dissolution enhancement. J Mol Liq. 2021;332:115909. https://doi.org/10.1016/j.molliq.2021.115909.
23. Binnemans K, Jones PT. Ionic liquids and Deep-Eutectic solvents in extractive metallurgy: mismatch between academic research and industrial applicability. J Sustain Metall. 2023;9:423–38. https://doi.org/10.1007/s40831-023-00681-6.
24. Sari IP, Zulaicha AS, Triyanti SB. Choline chloride based deep eutectic solvents: physicochemical properties and spectroscopic insights. Analit : Anal Environ Chem. 2024;9. https://doi.org/10.23960/analit.v9i02.200.
25. Lomba L, Werner Á, Giner B, Lafuente C. Deep eutectic solvents formed by glycerol and Xylitol, Fructose and sorbitol: effect of the different sugars in their physicochemical properties. Molecules. 2023. https://doi.org/10.3390/molecules28166023.
26. Zhao B-Y, Xu P, Yang F-X, Wu H, Zong M-H, Lou W-Y. Biocompatible deep eutectic solvents based on choline chloride: characterization and application to the extraction of Rutin from sophora Japonica. ACS Sustain Chem Eng. 2015;3:2746–55. https://doi.org/10.1021/acssuschemeng.5b00619.
27. Li J, Xu T, Liu J, Wen J, Gong S. Bioleaching metals from waste electrical and electronic equipment (WEEE) by Aspergillus niger: a review. Environ Sci Pollut Res. 2021;28:44622–37. https://doi.org/10.1007/s11356-021-15074-z.
28. Bastug A. 1:1 binary complexes of citric acid with some metal ions: stability and thermodynamic parameters. Rev Inorg Chem. 2007. https://doi.org/10.1515/REVIC.2007.27.1.53.
29. Jabłońska-Wawrzycka A, Rogala P, Michałkiewicz S, Hodorowiczb M, Barszcza B. Ruthenium complexes in different oxidation states: synthesis, crystal structure, spectra and redox properties. Dalton Trans. 2013;42:6092–101. https://doi.org/10.1039/C3DT32214A.
30. Cerrillo-Gonzalez MdM, Paz-Garcia JM, Muñoz-Espinosa M, Rodriguez-Maroto JM, Villen-Guzman M. Extraction and selective precipitation of metal ions from LiCoO2 cathodes using citric acid. J Power Sources. 2024;592:233870. https://doi.org/10.1016/j.jpowsour.2023.233870.
31. Wu Z, Zhang C, Yuan F, Lyu M, Yang P, Zhang L, Zhou M, Wang L, Zhang S, Wang L. Ni-rich cathode materials for stable high-energy lithium-ion batteries. Nano Energy. 2024;126:109620. https://doi.org/10.1016/j.nanoen.2024.109620.
32. Banerjee H, Grey CP, Morris AJ. Stability and redox mechanisms of Ni-Rich NMC cathodes: insights from First-Principles Many-Body calculations. Chem Mater. 2024;36:6575–87. https://doi.org/10.1021/acs.chemmater.4c00928.
33. Liao C, Li F, Liu J. Challenges and modification strategies of Ni-Rich cathode materials operating at High-Voltage. Nanomaterials (Basel). 2022;12. https://doi.org/10.3390/nano12111888.
34. Khalid HM, Santos RM. Deep eutectic solvents and ionic liquids in hydrometallurgical recovery of metals - A review of recent advances and challenges. Hydrometallurgy. 2025;238:106571. https://doi.org/10.1016/j.hydromet.2025.106571.
35. Panda P, Mishra S. Optimization of leaching of lithium and Cobalt from spent lithium-ion batteries by the choline chloride-citric acid/malonic acid DES using response surface methodology. Environ Res. 2025;269:120917. https://doi.org/10.1016/j.envres.2025.120917.
36. Schiavi P.G., Altimari P., Sturabotti E., Giacomo Marrani A., Simonetti G., Pagnanelli F. Decomposition of deep eutectic solvent aids metals extraction in Lithium-Ion batteries recycling. Chemsuschem. 2022;15:e202200966. https://doi.org/10.1002/cssc.202200966.
37. Svärd M, Ma C, Forsberg K, Schiavi PG. Addressing the reuse of deep eutectic solvents in Li-Ion battery recycling: insights into dissolution Mechanism, metal Recovery, regeneration and Decomposition, chemsuschem, 17 (2024) e202400410, https://doi.org/10.1002/cssc.202400410
38. Yu L, Ji X, Xu X, Xu C, Qi X, Wang G, Zhang S, Cai J, Lv G, Yang Z, Cheng Z, Li T, Pu Y, Jia Y. Sustainable and selective recovery of copper from electroplating sludge via choline chloride-citric acid deep eutectic solvent: mechanistic Elucidation and process intensification. Sep Purif Technol. 2025;376:134195. https://doi.org/10.1016/j.seppur.2025.134195.
39. Kityk A, Pavlik V, Hnatko M. Reshaping the future of battery waste: deep eutectic solvents in Li-ion battery recycling. J Energy Storage. 2024;97:112990. https://doi.org/10.1016/j.est.2024.112990.
40. Zheng S, Xu S, Wang Z, Duan H, Chen D, Long M, Li Y. Efficient leaching of valuable metals from spent lithium-ion batteries using green deep eutectic solvents: process optimization, mechanistic analysis, and environmental impact assessment. J Clean Prod. 2024;480:144128. https://doi.org/10.1016/j.jclepro.2024.144128.
41. Li B, Li Q, Wang Q, Yan X, Shi M, Wu C. Deep eutectic solvent for spent lithium-ion battery recycling: comparison with inorganic acid leaching. Phys Chem Chem Phys. 2022;24:19029–51. https://doi.org/10.1039/D1CP05968H.
42. Davis K, Demopoulos GP. Hydrometallurgical recycling technologies for NMC Li-ion battery cathodes: current industrial practice and new R&D trends. RSC Sustain. 2023;1:1932–51. https://doi.org/10.1039/D3SU00142C.

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